

EMULSIFIED WATER/HYDROCARBON FUEL, PREPARATION  
AND USES THEREOF

5      BACKGROUND OF THE INVENTION

The present invention relates to a fuel composed of an emulsion of water and of liquid hydrocarbons which is intended to be used in heat engines and thermal machines. More specifically, the present invention relates to an emulsified water/hydrocarbon fuel, the content of certain paraffins in the hydrocarbon phase of which makes it possible to reduce emissions during combustion.

For several years, the majority of oil companies have been working on the development of fuels (and in particular of engine fuels) comprising substitution products for hydrocarbons of petroleum origin, with a view both to economizing on hydrocarbons and to limiting pollution. Thus, water very quickly appeared as a particularly advantageous partial substituent, provided that it is maintained in a stable emulsion with the hydrocarbons.

Thus, patent applications WO 93/18117, WO 97/34969 and WO 01/48123 disclose fuels composed of a mixture generally comprising at least 5% by weight of water and hydrocarbons, maintained in emulsion by virtue of the use of specific compositions comprising surfactant additives. In comparison with a conventional engine fuel composed solely of hydrocarbons, these fuels make it possible, during combustion in a diesel engine, to reduce the emissions of polluting compounds, such as, in particular, nitrogen oxides, carbon monoxide, solid particles and nonincinerated hydrocarbons.

Patent application DE 3023372 discloses an engine fuel for diesel engines composed of an emulsion comprising at least 80% by volume of hydrocarbons and from 12 to 20% by volume of water, as well as from 0.5 to 1.5% by volume of an emulsifying agent which is an ether of alkylphenol and of polyglycol. The hydrocarbons are a

5 mixture of at least 10% by volume of a "middle oil" (of the conventional diesel fuel type) and of at most 90% by volume of a "heavy oil" which can be composed in particular, in all or part, of vegetable oil. The main advantage of this engine fuel is that it makes it possible to achieve a substantial saving with regard to the hydrocarbon fractions on which conventional diesel fuels are based by partially substituting them by two other constituents (water and vegetable oils).

10 SUMMARY OF THE INVENTION

15 The aim of the present invention is to provide an emulsified fuel based on hydrocarbons and on water which makes it possible to further reduce polluting emissions in comparison with the emulsified engine fuels known in the prior art.

20 This is because the applicant company has discovered that, surprisingly, these emissions could be substantially reduced provided that the hydrocarbons participating in the composition of the emulsion comprise a substantial amount of a specific family of paraffins, namely C<sub>8</sub> to C<sub>22</sub> normal paraffins (linear paraffins) (that is to say, the backbone of which is composed of 8 to 22 carbon atoms). Mixtures of such normal paraffins are envisaged.

25 To this end, the present invention provides an emulsified fuel comprising a hydrocarbon liquid phase, an aqueous phase and at least one emulsifying additive and exhibiting a water/hydrocarbons ratio by weight ranging from 5/95 to 35/65. This fuel is characterized in that 30 the hydrocarbon phase comprises from 5 to 35% by weight of C<sub>8</sub> to C<sub>22</sub> normal paraffins.

35 In comparison with the known emulsified fuels, the fuel according to the present invention makes it possible to significantly reduce emissions during combustion in a heat engine or a boiler, in particular emissions of nitrogen oxides and of solid particles. This effect becomes greater when said normal paraffins are C<sub>13</sub> to C<sub>19</sub> normal paraffins. Thus, according to a preferred

embodiment, the hydrocarbon phase comprises from 5 to 35% by weight of C<sub>13</sub> to C<sub>19</sub> normal paraffins.

Furthermore, the presence in the hydrocarbon phase of the above normal paraffins proved to have a particularly beneficial effect on the autoignition delay time and the cetane number of the fuel. This advantage is particularly noticeable when said fuel is an engine fuel for diesel vehicles, since these parameters represent the quality of the combustion of the engine fuel in a standard diesel engine. The implementation of the invention makes it possible, in comparison with an otherwise identical conventional water/hydrocarbon emulsion, to gain up to 10 cetane number points.

This effect is all the more advantageous as the normal paraffins under consideration in the invention have proved to have, with regard to the increase in the cetane number, a synergistic effect with the additives conventionally employed to increase the cetane number of diesel engine fuels, or "cetane number improvers" (generally alkyl nitrates or organic peroxides). The invention thus makes it possible, at an equal content of cetane number improver, to obtain more efficient engine fuels. The invention also makes it possible to reduce the content of cetane number improver in the engine fuel. In other words, the invention makes it possible to obtain fuels exhibiting an excellent combustion quality without using higher contents of cetane number improvers capable of negatively interacting with the other additives or having undesirable side effects when they are used at high doses.

Finally, the present invention has proved to have a beneficial effect on the stability of the emulsion as measured by centrifuging according to the standard NF M07 101. In particular, the stability on storage, both at ambient temperature and under hot conditions (75°C), is substantially improved.

The emulsified fuel according to the invention comprises a hydrocarbon liquid phase and an aqueous

phase. Preferably, the water/hydrocarbons ratio by weight is between 8/92 and 20/80.

According to the invention, the hydrocarbon phase comprises from 5 to 35% by weight of C<sub>8</sub> to C<sub>22</sub> normal paraffins. Advantageously, said hydrocarbon phase comprises from 8 to 20% by weight and preferably from 10 to 20% by weight of said C<sub>8</sub> to C<sub>22</sub>, preferably C<sub>13</sub> to C<sub>19</sub>, normal paraffins.

The hydrocarbon phase can be composed of any mixture of hydrocarbons, provided that it comprises the required normal paraffins in an appropriate amount.

According to a first embodiment of the invention, the hydrocarbon phase comprises at least one petroleum fraction of gasoline, diesel fuel or kerosene type selected so that it comprises from 5 to 35% by weight, preferably from 8 to 20% by weight, more preferably still from 10 to 20% by weight of C<sub>8</sub> to C<sub>22</sub>, preferably C<sub>13</sub> to C<sub>19</sub>, normal paraffins.

According to a second embodiment, which is the preferred embodiment, the hydrocarbon phase is composed of a conventional hydrocarbon engine fuel to which at least one fraction rich in normal paraffins has been added. The hydrocarbon phase then comprises a mixture composed of one or more hydrocarbon fractions and of at least one fraction rich in C<sub>8</sub> to C<sub>22</sub>, preferably C<sub>13</sub> to C<sub>19</sub>, normal paraffins. The term "rich" is understood to mean that said fraction comprises at least 50% by weight of said normal paraffins, preferably at least 80% by weight, more preferably still at least 90% by weight.

The said fraction rich in normal paraffins is then mixed with the hydrocarbon fraction(s) according to their respective contents of normal paraffins, in proportions such that the resulting hydrocarbon phase comprises from 5 to 35% by weight, preferably from 8 to 20% by weight, more preferably still from 10 to 20% by weight of C<sub>8</sub> to C<sub>22</sub>, preferably C<sub>13</sub> to C<sub>19</sub>, normal paraffins.

Said fraction rich in normal paraffins can have various origins.

It can be, according to a first alternative form, a fraction of petroleum origin obtained during oil refining operations. Some fractions, such as gasolines, kerosenes, indeed even light diesel fuels, can, in a way known per se, include large amounts of normal paraffins. Mention may be made, as nonlimiting examples, of straight-run gasolines, kerosenes and distillates (resulting directly from the distillation of crude oil), or those resulting from catalytic cracking, hydrocracking or hydrotreating processes. It is then possible to fractionate such fractions by distillation, so as to isolate a fraction including a substantial amount of the normal paraffins required in the present invention. It is possible in particular, starting from such fractions, to isolate the normal paraffins using appropriate molecular sieves, which make it possible to separate the normal paraffins from the other hydrocarbons (in particular isoparaffins), and to thus prepare fractions of petroleum origin comprising at least 80% by weight of the required normal paraffins.

According to a second alternative form, said fraction rich in normal paraffins comprises synthetic paraffins obtained by oligomerization of olefins comprising from 2 to 5 carbon atoms or by the Fischer-Tropsch synthesis starting from light hydrocarbons, such as methane or natural gas.

According to a third particularly advantageous alternative form, said fraction rich in normal paraffins comprises at least one hydrotreated animal or vegetable oil and/or fat. This is because, in a way known per se, complete hydrotreating of the fatty acid triglycerides present in animal or vegetable fatty substances makes it possible, by hydrocracking of the triglyceride structure and complete hydrogenation of the fatty acids, to obtain normal paraffin fractions in a particularly pure form, that is to say virtually devoid of other hydrocarbons. By appropriately choosing the starting oils or fats, in particular according to the length and the structure of

the fatty acids, and by applying a treatment comprising a hydrotreating under appropriate conditions, followed by fractionation (generally by distillation) of the effluents, it is possible to obtain fractions very rich  
5 in C<sub>8</sub> to C<sub>22</sub> normal paraffins.

The starting oil or fat can advantageously be chosen from:

10 vegetable oils, such as, for example, rapeseed oil, soybean oil, sunflower oil, palm oil, canola oil or oils extracted from resinous trees (in particular resinous conifers);

animal fats, such as, for example, purified fats (yellow grease), tallow or poultry fats;

15 waste food oils or fats, such as those recovered from the catering industry, which generally comprise a mixture of animal fats and vegetable oils;

and the mixtures of the above products.

20 The operating conditions under which these oils or fats are converted to paraffins comprise a key stage of hydrotreating in the presence of a catalyst based on transition metals, at a temperature preferably of between 350 and 450°C and a hydrogen pressure ranging from 4 MPa to 15 MPa. The effluents are then recovered and fractionated, so as to obtain the desired normal  
25 paraffins. Use may be made, for example, of the processes as disclosed in patents US 4 992 605 and US 5 705 722.

It is, of course, possible to combine the three alternative forms described above and to simultaneously incorporate, in the hydrocarbon phase, a fraction rich in  
30 normal paraffins of petroleum origin and/or a fraction rich in normal paraffins comprising synthetic paraffins and/or a fraction rich in normal paraffins based on hydrotreated animal or vegetable oil or fat.

It is possible to employ, as hydrocarbon fraction  
35 with which the fraction rich in normal paraffins is mixed in order to obtain the hydrocarbon phase according to the invention, fractions and mixtures of fractions of very diverse origins and natures. This choice is essentially

dictated by the use for which the fuel is intended, by the availability of the various hydrocarbon fractions and by economic considerations (cost of the fuel).

When the fuel is intended for use as engine fuel for  
5 heat engines, the hydrocarbon fraction, with which the fraction rich in normal paraffins is mixed in order to obtain the hydrocarbon phase according to the invention, is advantageously chosen from the bases which are constituents of the composition of conventional engine  
10 fuels and which comprise in particular gasoline fractions (distillation range generally within the span 25 to 200°C), middle distillates, such as, for example, kerosene fractions (distillation range generally within the span 160 to 240°C) and diesel fuel fractions  
15 (distillation range generally within the span 160 to 400°C), biofuels, and the mixtures of such fractions. These fractions can result from oil refining or from agriculture (case of biofuels) or can be synthetic hydrocarbons.

20 The term "biofuel" denotes light alcohols, such as ethanol, oils of vegetable or animal origin, and the esters of such oils. The hydrocarbon phase of the fuel according to the invention can thus advantageously comprise from 0.1 to 60% by weight and preferably from  
25 0.5 to 50% by weight of biofuel. The preferred biofuels are the esters of alcohols comprising from 1 to 4 carbon atoms and of fatty acids or of mixtures of fatty acids comprising from 16 to 22 carbon atoms. The particularly preferred biofuels are the methyl esters of vegetable  
30 oils, such as, for example, but not limitingly, soybean oil, rapeseed oil, sunflower oil, olive oil or palm oil.

When the fuel is intended for other uses, the hydrocarbon fraction, with which the fraction rich in normal paraffins is mixed in order to obtain the hydrocarbon phase according to the invention, can be chosen from the fractions mentioned above for the engine  
35 fuels but also from intermediate vacuum distillates (distillation range generally within the span 350 to

450°C), heavy vacuum distillates (distillation range generally within the span 400 to 550°C), indeed even bottom cuts, and generally from all the fractions conventionally employed in fuels, such as, for example, 5 FFOs (Furnace Fuel Oils), fuel oils, heating oils, heat oils, and the mixtures of such fractions.

The engine fuel according to the invention exists in the form of an emulsion of fine droplets of aqueous phase evenly dispersed in the hydrocarbon phase. 10 Advantageously, the mean diameter of the droplets of aqueous phase evenly dispersed in the hydrocarbon phase is less than or equal to 5 µm, preferably less than or equal to 3 µm, more preferably still less than or equal to 1 µm. Preferably, the particle size profile of the 15 drop sizes is of the type monodispersed around a value of approximately 0.5 µm. The above values for mean size of the droplets correspond to measurements carried out by the laser particle sizing technique.

In order for the emulsion to be stable over time 20 (that is to say, in order for the water droplets to remain homogeneously dispersed in the hydrocarbon phase and to prevent their coalescence, eventually resulting in the separation of the aqueous phase and the organic phase), it comprises at least one emulsifying agent. The 25 term "emulsifying agent" denotes any additive or mixture of additives having surfactant properties capable of guaranteeing the stability of the fine droplets of aqueous phase in the organic phase. Numerous additives can be employed for this purpose, in particular ionic or 30 nonionic emulsifiers of synthetic or natural origin, such as, for example, but not limitingly, compounds chosen from fatty acids, fatty acid derivatives, fatty alcohols, ethoxylated fatty amines, polyol esters, functionalized polymers, and their mixtures.

Advantageously, the emulsifying agent comprises at 35 least one nonionic organic emulsifying additive preferably of natural origin. Mention may be made, as examples, of fatty acids and their derivatives, polyol

esters or functionalized polymers.

In a particularly advantageous way, the emulsifying agent is composed of a mixture of at least two emulsifying additives. Examples of such emulsifying agents are disclosed in patent applications WO 97/34969 and WO 01/48123.

The content of emulsifying agent in the fuel depends, in a way known per se, on the nature and on the effectiveness of this agent. Generally, the additives used as emulsifying agents are generally incorporated in the emulsions at contents which can range from 0.5 to 5% by weight. Preferably, the fuel according to the invention exhibits a content of emulsifying agent of between 1 and 3% by weight.

The emulsified fuel according to the present invention can advantageously comprise one or more biocidal agents, preferably in its aqueous phase. This biocidal agent is preferably a bactericide and/or a fungicide. Mention may be made, as nonlimiting examples of biocidal agents, of isothiazolones and their chlorinated derivates, benzalkonium chlorides, organic peroxides or isothiocyanates.

The emulsified fuel can also comprise at least one antifreeze. Use may be made, as antifreezes, for example, of alcohols, glycols, derivatives of glycols or of alcohols, or saline solutions.

It can also comprise at least one soot remover. Mention may be made, as examples of such removers, of the additives composed of one or more metal or alkaline earth metal catalysts capable of promoting soot postcombustion reactions. The preferred catalysts are based on magnesium, calcium, barium, cerium, copper, iron or their mixtures. These catalytic promoters of the destruction of soot are also easy to introduce as they are generally compounds whose salts are soluble in water and thus in the aqueous phase of the emulsions according to the invention.

When the fuel is intended for use as engine fuel for

heat engines, its sulfur content, determined according to the standard NF M 07-100, is preferably less than or equal to 350 ppm, preferably less than or equal to 50 ppm and more preferably still less than or equal to 10 ppm.

5 When the fuel is intended for use as fuel for thermal machines, its sulfur content, determined according to the standard NF M 07-100, is preferably less than or equal to 1% by weight, preferably less than or equal to 2% by weight and more preferably still less than or equal to 10 0.1% by weight.

15 Whatever its use, the content of polycyclic aromatic hydrocarbons in the fuel according to the invention, determined according to the standard IP 391, is preferably less than or equal to 11% by weight, more 15 preferably less than or equal to 6% by weight.

20 Furthermore, for use as engine fuel, the emulsified fuel according to the invention preferably comprises one or more other additives which can be any additive conventionally employed in engine fuels, including, for example, but not limitingly:

25 - one or more cetane number improvers, such as, for example, alkyl nitrates, in which the saturated or unsaturated and linear or branched (preferably saturated and branched) alkyl radical comprises from 3 to 20 and preferably from 5 to 15 carbon atoms (in particular 2-ethylhexyl nitrate), or organic peroxides and in particular aryl peroxides, in which the aryl group is a benzyl group or a substituted benzyl group (for example benzoyl peroxide), or alkyl peroxides, in which the 30 saturated or unsaturated and linear or branched (preferably saturated and branched) alkyl radical comprises from 2 to 20 and preferably from 2 to 15 carbon atoms (for example tert-butyl peroxide);

35 - one or more flow improvers, such as, for example, ethylene/vinyl acetate (EVA), ethylene/vinyl propionate (EVP), ethylene/vinyl ethanoate (EVE), ethylene/methyl methacrylate (EMMA) or ethylene/alkyl fumarate copolymers;

- one or more antifoaming agents, such as, for example, polysiloxanes, oxyalkylated polysiloxanes, or fatty acid amides;
- 5 - one or more detergent additives and/or corrosion inhibitors, such as, for example, amines, succinimides, alkenylsuccinimides, polyalkylamines, polyalkylpolyamines and polyetheramines;
- 10 - one or more slip additives or antiwear additives, such as, for example, fatty acids and their ester or amide derivatives or mono- and polycyclic carboxylic acids and their ester or amide derivatives;
- 15 - one or more cloud point additives, such as, for example, olefin comprising a long chain/(meth)acrylic ester/maleimide terpolymers or fumaric or maleic acid ester derivatives;
- one or more additives for combating sedimentation, such as, for example, (meth)acrylic acid/alkyl (meth)acrylate copolymers where the alkyl group is amidated by a polyamine, polyamine alkenylsuccinimides, or derivatives of phthalamic acid and of fatty amine comprising a double chain;
- 20 - one or more polyfunctional additives for operability under cold conditions, such as, for example, polymers based on olefin and on alkenyl nitrate.

25 In particular, as was set out above, due to the synergistic effect observed between the C<sub>8</sub> to C<sub>22</sub> normal paraffins and the cetane number improvers, the emulsified fuel according to the invention makes it possible to reduce the levels of incorporation of such improvers or, 30 at the same level of cetane number improver, to obtain more efficient engine fuels. This synergistic effect is particularly effective when the ratio of the content by weight of C<sub>8</sub> to C<sub>22</sub> (preferably C<sub>13</sub> to C<sub>19</sub>) normal paraffins in the hydrocarbon phase to the content by 35 weight of cetane number improvers in the engine fuel is between 5/0.5 and 15/0.5, preferably between 5/0.3 and 15/0.1.

The fuel according to the invention can be prepared

in various ways and in particular by any conventional way for preparing emulsions.

Advantageously, the hydrocarbon phase is prepared beforehand, before emulsifying the latter with the aqueous phase.

The invention thus also provides a process for the preparation of an emulsified fuel comprising at least the following stages:

(a) selecting at least one petroleum fraction of gasoline, diesel fuel or kerosene type comprising from 5 to 35% by weight, preferably from 8 to 20% by weight, more preferably still from 10 to 20% by weight of C<sub>8</sub> to C<sub>22</sub>, preferably C<sub>13</sub> to C<sub>19</sub>, normal paraffins; or

(a') mixing one or more hydrocarbon fractions and at least one fraction comprising at least 50% by weight of C<sub>8</sub> to C<sub>22</sub>, preferably C<sub>13</sub> to C<sub>19</sub>, normal paraffins, so as to obtain a hydrocarbon phase comprising from 5 to 35% by weight, preferably from 8 to 20% by weight, more preferably still from 10 to 20% by weight of C<sub>8</sub> to C<sub>22</sub>, preferably C<sub>13</sub> to C<sub>19</sub>, normal paraffins; then

(b) emulsifying, in the presence of at least one emulsifying agent, the hydrocarbon phase obtained in (a) or (a') with an aqueous phase according to a water/hydrocarbons ratio by weight ranging from 5/95 to 35/65.

The emulsification proper, and the incorporation of the various additives (including the emulsifying agent), can be carried out in various ways.

It is advantageous to mix all or a portion of the additives with one and/or other of the phases, prior to the emulsification. For example, stage (b) can be carried out in the way disclosed in patent application WO 00/34419 by mixing the emulsifying agent with the hydrocarbon phase and then passing the resulting mixture one or more times into an emulsifier system fed with the water necessary for the formation of the emulsion.

It is also advantageous to carry out stage (b) in the way disclosed in patent application WO 01/36569, by:

(b1) premixing the water and the emulsifying agent, followed by dispersion in the hydrocarbon phase, or simultaneous mixing of the hydrocarbon phase with the water and the emulsifying agent; then

5 (b2) emulsifying proper using an appropriate device, for example chosen from rotor-stators, emulsifier apparatuses, static mixers or in-line turbine systems.

The emulsified fuel according to the present invention can be employed in various applications. It can  
10 be employed in particular as engine fuel for heat engines or as fuel for fuel cells. Its use as engine fuel for diesel engines is particularly advantageous.

The fuel according to the invention can also be used  
15 as fuel for thermal machines, such as, for example, industrial or domestic boilers, furnaces, turbines or generators. A particularly advantageous use is that as FFOs (or Furnace Fuel Oils), that is to say as fuel for domestic boilers.

Finally, the invention provides a method for reducing  
20 the emissions from heat engines or thermal machines, comprising the use of an emulsified fuel as described above.

#### DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

The examples below are targeted at illustrating the  
25 invention, without limiting the scope thereof.

##### Example 1:

Use is made, as reference hydrocarbon liquid phase P1, of a conventional diesel fuel fraction which has the  
30 following properties:

Content of C<sub>13</sub> to C<sub>19</sub> normal paraffins: 4% by weight

Distillation range (standard ASTM D86)

initial point: 179°C

10 vol % point: 201°C

35 50 vol % point: 254°C

90 vol % point: 331°C

final point: 360°C

Sulfur content (standard ASTM D5453): 218 ppm

Nitrogen content (standard ASTM D4629) : 189 ppm

Content of aromatic compounds (standard ASTM D5186) :  
10.5 vol %

Viscosity at 40°C (standard ASTM D445) : 2.59 cSt

5 A second hydrocarbon phase P2 is prepared from P1 by mixing 74.1 parts by weight of P1 with 6 parts by weight of a fraction rich in normal paraffins of petroleum origin composed to more than 99% by weight of C14 normal paraffin. The content of C13 to C19 normal paraffins in  
10 the hydrocarbon phase P2 thus obtained is 11.2% by weight.

15 The respective emulsified fuels A1 and A2 are prepared from P1 and P2 by emulsifying 80.1% by weight of the respective hydrocarbon phases P1 and P2 with 17.4% by weight of water in the presence of 2.5% by weight of emulsifying agent. The emulsifying agent employed for this purpose is composed of a mixture of three surfactant additives, namely an ester of fatty acid and sorbitan, an ethoxylated fatty acid and an ethoxylated fatty alcohol.

20 The emulsions A1 and A2 are tested as engine fuel on a "Detroit Diesel Corporation Series 60" diesel engine according to the test and emission measurement procedures described in the "California Exhaust Emission Standards and Test Procedures for 1985 and Subsequent Model Heavy-Duty Diesel Powered Engines and Vehicles", as  
25 incorporated by reference in the California Code of Regulations, Title 13, Section 1956.8(b).

30 During these tests, it is found that, in comparison with the reference emulsified engine fuel A1, the emulsified engine fuel A2 according to the invention makes it possible to reduce emissions of nitrogen oxides by 3%.

Example 2:

35 This example illustrates the synergistic effect which is exerted over the increase in the cetane number of the water/hydrocarbon emulsions when the emulsion comprises both the C<sub>8</sub> to C<sub>22</sub> normal paraffins considered in the invention and a (or several) cetane number improver.

Four emulsified water/hydrocarbons engine fuels (A3 to A7) are prepared from the same reference diesel fuel G. All these emulsions exhibit a water/hydrocarbons ratio by weight of 10/90 and comprise 2% by weight of an emulsifying agent composed of a mixture of three surfactant additives, namely an ester of fatty acid and of sorbitan, an ethoxylated fatty acid and an ethoxylated fatty alcohol.

In the emulsions A3 and A4, the hydrocarbon phase is composed to 100% of the diesel fuel G. In the emulsions A5 and A6, the hydrocarbon phase is composed of a mixture of 90% by weight of diesel fuel G and of 10% by weight of a fraction C rich in normal paraffins. The fraction C is composed of hydrotreated animal fats and comprises more than 95% by weight of C<sub>8</sub> to C<sub>22</sub> normal paraffins with a predominance of C<sub>15</sub> to C<sub>18</sub> (inclusive) normal paraffins.

0.2% by weight (with respect to the total weight of the emulsion) of a conventional cetane number improver, composed of 2-ethylhexyl nitrate, is added to the emulsions A4 and A6.

The cetane number of each of the emulsified engine fuels A3 to A6 was measured in accordance with the method described in the standard ASTM D613. The compositions of the emulsified engine fuels are summarized in table I below, which also gives the cetane numbers obtained for each.

Table I

Emulsion	Hydrocarbon phase composition (% by weight)	Content of cetane number improver in the emulsion (% by weight)	Cetane number measured (standard ASTM D613)	Cetane increase/A3
A3	100% G	0%	43.2	-
A4	100% G	0.2%	48.7	5.5
A5	90% G + 10% C	0%	46.4	3.2
A6	90% G + 10% C	0.2%	53	9.8

The above results show that, while the incorporation

in the emulsified engine fuel of a cetane number improver or of a fraction C rich in C<sub>8</sub> to C<sub>22</sub> normal paraffins makes it possible to increase the cetane number of the engine fuel (cf. the emulsions A4 and A5, which respectively comprise the cetane number improver and the fraction C and which have cetane numbers greater by 5.5 and 3.2 points respectively with respect to the emulsion A3 which comprises neither one nor the other), the joint incorporation of these two components in the emulsified engine fuel makes it possible to obtain a cetane number increase which is greater than the sum of the individual increases (cf. the emulsion A6, which comprises both the cetane number improver and the fraction C and for which the cetane number increase is 9.8, i.e. 1.1 points more than the sum of the increases obtained for A4 and A5, i.e. 8.7).

In other words, the presence in the hydrocarbon phase of a high content of C<sub>8</sub> to C<sub>22</sub> normal paraffins makes it possible to significantly increase the effect of the cetane number improver. Specifically, in the conventional emulsion A3, the addition of 0.2% by weight of cetane number improver makes it possible to increase the cetane number by 5.5 points, whereas, in the emulsion A5 according to the invention, the addition of 0.2% by weight of cetane number improver makes it possible to increase the cetane number by 6.6 points. The invention thus makes it possible, at a constant content of cetane number improver, to enhance the performance of the emulsified engine fuel or, at a constant performance, to reduce the contents of cetane number improver.

Thus, the presence in the emulsions according to the invention of high contents of C<sub>8</sub> to C<sub>22</sub> normal paraffins in conjunction with the use of a conventional cetane number improver provides a true synergistic effect with regard to the cetane number of the emulsified engine fuel.

Example 3:

This example illustrates the improvement in the

stability of the emulsified fuels according to the invention.

The stability of the emulsified engine fuels A3 and A5 of example 2 was determined at ambient temperature in 5 accordance with the centrifuging stability test described in the standard NF M07 101. The graph presented in figure 1 below illustrates the results obtained in terms of sedimentation of the engine fuel (i.e. phase separation of the emulsion) during the centrifuging time. The 10 greater the degree of sedimentation, the more unstable the emulsion.

The results presented in figure 1 clearly illustrate the beneficial effect, in terms of stability of the emulsion, of the presence in the hydrocarbon phase of a 15 significant content of C<sub>8</sub> to C<sub>22</sub> normal paraffins: the emulsion A5, in the hydrocarbon phase of which a fraction C rich in C<sub>8</sub> to C<sub>22</sub> normal paraffins has been incorporated in accordance with the invention, exhibits a markedly better stability than that of the emulsion A3, the 20 hydrocarbon phase of which is composed solely of a conventional diesel fuel.

WHAT IS CLAIMED IS:

1. An emulsified fuel comprising a hydrocarbon liquid phase, an aqueous phase and at least one emulsifying agent and exhibiting a water/hydrocarbons ratio by weight ranging from 5/95 to 35/65, characterized in that the hydrocarbon phase comprises from 5 to 35% by weight of C<sub>8</sub> to C<sub>22</sub> normal paraffins, the aqueous phase being dispersed in the hydrocarbon phase.
- 10 2. The fuel as claimed in claim 1, characterized in that the hydrocarbon phase comprises from 5 to 35% by weight of C<sub>13</sub> to C<sub>19</sub> normal paraffins.
- 15 3. The fuel as claimed in claim 1 or claim 2, characterized in that the hydrocarbon phase comprises from 8 to 20% by weight of said C<sub>8</sub> to C<sub>22</sub>, preferably C<sub>13</sub> to C<sub>19</sub>, normal paraffins.
- 20 4. The fuel as claimed in any one of claims 1 to 3, characterized in that the hydrocarbon phase comprises from 10 to 20% by weight of said C<sub>8</sub> to C<sub>22</sub>, preferably C<sub>13</sub> to C<sub>19</sub>, normal paraffins.
- 25 5. The fuel as claimed in any one of claims 1 to 4, characterized in that the hydrocarbon phase comprises at least one petroleum fraction of gasoline, diesel fuel or kerosene type.
- 30 6. The fuel as claimed in any one of claims 1 to 4, characterized in that the hydrocarbon phase comprises a mixture composed of one or more hydrocarbon fractions and of at least one fraction rich in said normal paraffins, that is to say comprising at least 50% by weight of said normal paraffins.
- 35 7. The fuel as claimed in claim 6, characterized in that said fraction rich in normal paraffins is a fraction

of petroleum origin.

8. The fuel as claimed in claim 6 or claim 7, characterized in that said fraction rich in normal paraffins comprises synthetic paraffins obtained by oligomerization of olefins comprising from 2 to 5 carbon atoms or by the Fischer-Tropsch synthesis starting from light hydrocarbons.

10 9. The fuel as claimed in any one of claims 6 to 8, characterized in that the said fraction rich in normal paraffins comprises at least one hydrotreated animal or vegetable oil and/or fat.

15 10. The fuel as claimed in claim 9, characterized in that the oil and/or the fat is chosen from:

vegetable oils;  
animal fats;  
waste food oils or fats;  
20 and the mixtures of the above products.

11. The fuel as claimed in any one of claims 6 to 10, characterized in that the hydrocarbon fraction, with which the fraction rich in normal paraffins is mixed in order to obtain said hydrocarbon phase, is chosen from gasoline fractions, middle distillates, preferably chosen from kerosene fractions and diesel fuel fractions, biofuels, preferably chosen from esterified or nonesterified vegetable oils, and the mixtures of such fractions.

30 12. The fuel as claimed in any one of claims 6 to 11, characterized in that the hydrocarbon fraction, with which the fraction rich in normal paraffins is mixed in order to obtain said hydrocarbon phase, comprises at least one fraction chosen from intermediate vacuum distillates, heavy vacuum distillates or bottom cuts.

13. The fuel as claimed in any one of claims 1 to 12, characterized in that its content of emulsifying agent is between 0.5 and 5% by weight.

5       14. The fuel as claimed in any one of claims 1 to 13, characterized in that the emulsifying agent comprises at least one nonionic organic emulsifying agent, preferably of natural origin, preferably chosen from fatty acids and their derivatives, polyol esters or functionalized polymers.

10      15. The fuel as claimed in any one of claims 1 to 14, characterized in that it comprises a bactericide and/or a fungicide.

15      16. The fuel as claimed in any one of claims 1 to 15, characterized in that it comprises at least one antifreeze chosen from alcohols, glycols, derivatives of glycols or of alcohols, or saline solutions.

20      17. The fuel as claimed in any one of claims 1 to 16, characterized in that it comprises at least one soot remover preferably chosen from catalysts based on magnesium, calcium, barium, cerium, copper, iron or their mixtures.

25      18. The fuel as claimed in any one of claims 1 to 17, characterized in that it comprises at least one cetane number improver preferably chosen from alkyl nitrates or organic peroxides.

30      19. The fuel as claimed in claim 18, characterized in that the ratio of the content by weight of C<sub>8</sub> to C<sub>22</sub> normal paraffins in the hydrocarbon phase to the content by weight of cetane number improvers in the engine fuel is between 5/0.5 to 15/0.05, preferably between 5/0.3 and 15/0.1.

20. The fuel as claimed in any one of claims 6 to 18, characterized in that its sulfur content, determined according to the standard NF M 07-100, is less than or equal to 350 ppm and preferably less than or equal to 50 ppm.

21. The fuel as claimed in any one of claims 6 to 20, characterized in that its content of polycyclic aromatic hydrocarbons, determined according to the standard IP 391, is preferably less than or equal to 11% by weight, more preferably less than or equal to 6% by weight.

22. A process for the preparation of an emulsified fuel as claimed in any one of claims 1 to 21, characterized in that it comprises at least the following stages:

(a) selecting at least one petroleum fraction of gasoline, diesel fuel or kerosene type comprising from 5 to 35% by weight, preferably from 8 to 20% by weight, more preferably still from 10 to 20% by weight of C<sub>8</sub> to C<sub>22</sub>, preferably C<sub>13</sub> to C<sub>19</sub>, normal paraffins; or

(a') mixing one or more hydrocarbon fractions and at least one fraction comprising at least 50% by weight of C<sub>8</sub> to C<sub>22</sub>, preferably C<sub>13</sub> to C<sub>19</sub>, normal paraffins, so as to obtain a hydrocarbon phase comprising from 5 to 35% by weight, preferably from 8 to 20% by weight, more preferably still from 10 to 20% by weight of C<sub>8</sub> to C<sub>22</sub>, preferably C<sub>13</sub> to C<sub>19</sub>, normal paraffins; then

(b) emulsifying, in the presence of at least one emulsifying agent, the hydrocarbon phase obtained in (a) or (a') with an aqueous phase according to a water/hydrocarbons ratio by weight ranging from 5/95 to 35/65.

23. The process as claimed in claim 22, characterized in that stage (b) is carried out by mixing the emulsifying agent with the hydrocarbon phase and then passing the resulting mixture one or more times into an

emulsifier system fed with the water necessary for the formation of the emulsion.

24. The process as claimed in claim 22, characterized  
5 in that stage (b) is carried out by:

(b1) premixing the water and the emulsifying agent, followed by dispersion in the hydrocarbon phase, or simultaneous mixing of the hydrocarbon phase with the water and the emulsifying agent, then

10 (b2) emulsifying proper using an appropriate device.

25. The use of the emulsified fuel as claimed in any one of claims 1 to 21 as engine fuel, in particular as  
15 engine fuel for a diesel engine.

26. The use of the emulsified fuel as claimed in any one of claims 1 to 21 as fuel for thermal machines preferably chosen from industrial or domestic boilers,  
20 furnaces, turbines and generators.

27. The use of the emulsified fuel as claimed in any one of claims 1 to 21 as Furnace Fuel Oil.

25 28. A method for reducing emissions from heat engines or thermal machines, comprising the use of an emulsified fuel as claimed in any one of claims 1 to 21.

10/522419

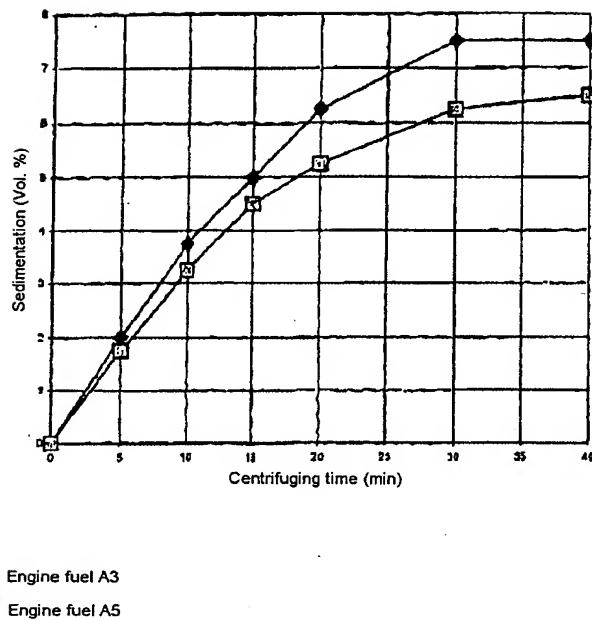


FIG 1

Best Available Copy